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Selection and Testing of Surfactants for Enhanced In Situ Alkaline Hydrolysis (S-ISAH) of Pesticide DNAPL

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Background. A 20,000 m² former chemical dump site in the northwestern part of Denmark is contaminated with 200 to 300 tons of organophosphorous pesticides and pesticide manufacturing wastes, a significant fraction of which consists of the highly toxic pesticide parathion. The majority of contaminant mass is present as sorbed phase and residual dense nonaqueous phase liquid (DNAPL). A European Commission-funded demonstration project (www.northpestclean.dk) was initiated in September 2010 with the objectives of determining the effectiveness of using in situ alkaline hydrolysis to treat the organophosphorous pesticide DNAPL. A primary challenge for effective treatment was in situ mixing, and establishing sufficient contact between DNAPL and hydroxide used to achieve alkaline conditions (pH 12) in the aqueous phase. Surfactants were tested as a novel method for enhancing treatment by in situ alkaline hydrolysis. The purpose of the surfactants is two-fold: to increase the solubility of the pesticides in the alkaline solution for increased hydrolysis, and increased mobility of the DNAPL by lowering the interfacial tension. The range of commercially available surfactant formulation is immense, and selection of formulations for further testing was challenging. Surfactants based on nonylphenol ethoxylate as active ingredient were initially identified as promising candidates, but these compounds are banned for use in Denmark due to concerns of their environmental fate, necessitating the selection of alternative surfactants.

Objectives/Approach. The objectives of this project were to select a surfactant formulation for further pilot-scale testing at the field site. First a literature search was conducted to identify of potential surfactants used under alkaline conditions in industry, and surfactants recommended by US EPA as alternatives to nonylphenol ethoxylates. Second, candidate surfactants were evaluated based on their stability under alkaline conditions, acceptability for in situ use, biodegradability and previous use for subsurface remediation. Laboratory experiments were performed in duplicate to test the effects of candidate surfactant formulations on the pesticide DNAPL solubility and reactivity under highly alkaline conditions at comparable surfactant concentration. Surfactant formulations with the best performing active ingredient groups were further tested at two concentrations with the presence of site soil. Eighteen parent compound and hydrolysis products were analyzed as evaluation parameters.

Results. Nine surfactant formulations, comprised nonionic, anionic, and amphoteric types from three suppliers, were identified in the theoretical selection process. The

formulations represented four groups of active ingredients, including alcohol ethoxylate, alkyl polyglycosides, alkane sulfonates and carboxylated propionate. The alcohol ethoxylate formulations showed the best performance with respect to solubility enhancement of the DNAPL, although no enhancement in the pesticide reactivity was observed. Subsequent batch studies with site soil revealed internal differences between the four nonionic ethoxylate formulations with respect to both solubility and reactivity. The best performance was obtained with the Ecosurf EH-9 and Tergitol 15-S-12 surfactant formulations; Ecosurf EH-9 was selected for pilot-scale testing at a concentration of 30 g/L. The pilot-scale testing is currently ongoing, and field results will be obtained shortly.